Journal of Environmental Quality SPECIAL SECTION
CELEBRATING THE 350TH ANNIVERSARY OF DISCOVERING PHOSPHORUS—FOR BETTER OR WORSE

Mechanisms Responsible for Soil Phosphorus Availability Differences between Sprinkler and Furrow Irrigation

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Abstract

From a historical perspective, human-induced soil erosion and resulting soil phosphorus (P) losses have likely occurred for thousands of years. In modern times, erosion risk and off-site P transport can be decreased if producers convert from furrow to sprinkler irrigation, but conversion may alter nutrient dynamics. Our study goal was to determine soil P dynamics in furrow- (in place since the early 1900s) versus sprinkler-irrigated (installed within the last decade) soils from four paired producer fields in Idaho. Furrow- and sprinkler-irrigated soils (0–5 cm; Aridisols) contained on average 38 and 20 mg kg^{-1} of Olsen-extractable P (i.e., plant-available P), respectively; extractable P values over 40 mg kg^{-1} limit Idaho producers to P application based on crop uptake only. Soil samples were also analyzed using a modified Hedley extraction. Furrow-irrigated soils contained greater inorganic P concentrations in the soluble+aluminum (Al)-bound+iron (Fe)-bound, occluded, and amorphous Fe-bound pools. Phosphorus *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy was unable to detect Fe-associated P but indicated greater amounts of apatite-like or octacalcium phosphate-like P in furrow-irrigated producer soils, while sprinkler-irrigated fields had lower amounts of apatite-like P and greater proportions of P bound to calcite. Findings from a controlled USDA-ARS sprinkler- versus furrow-irrigation study suggested that changes in P dynamics occur slowly over time, as few differences were observed. Overall findings suggest that Fe redox chemistry or changes in calcium (Ca)-associated P in flooded conditions altered P availability under furrow irrigation, even in aridic, calcareous soils, contributing to greater Olsen-extractable P concentrations in long-term furrow-irrigated fields.

Core Ideas

- Irrigation type may greatly affect soil P dynamics in calcareous systems.
- Furrow irrigated fields contained more plant-available P than sprinkler irrigated fields.
- Furrow irrigation leads to Fe chemistry alterations, release of P, and increases available P.
- Available P increases under furrow irrigation could limit amendment application based on P, not N, crop needs.
- We still do not fully understand P dynamics in irrigated calcareous systems.

J. Environ. Qual. 48:1–10 (2019)
doi:10.2134/jeq2019.01.0016
Supplemental material is available online for this article.
Received 17 Jan. 2019.
Accepted 14 May 2019.
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Human-induced irrigation events have occurred for thousands of years (Hillel, 1994), leading to surface water nutrient (e.g., P) enrichment, which is a serious problem in the United States (USEPA, 1996). In fact, the primary P loss pathway from agricultural soils is through surface runoff (Vadas et al., 2004), which may be enhanced by the use of certain irrigation systems. Furthermore, once in irrigation return flow waters, P may be transported distances greater than 18 km (Ippolito and Nelson, 2013). Thus, managing irrigation practices may help control runoff and consequently reduce P losses from agricultural systems.

Two major irrigation practices used in production agriculture are furrow and sprinkler irrigation. Furrow irrigation is a type of surface irrigation whereby furrows are created between crop rows and irrigation water flows down the furrows to provide water for plants. Sprinkler irrigation applies water through sprinkler heads or nozzles, creating small water droplets that fall onto soil. Sprinkler irrigation improves water use efficiency as compared to furrow irrigation (Al-Jamal et al., 2001), making sprinkler irrigation an attractive water conservation practice. Conservation efforts also suggest that increasing sprinkler and reducing furrow irrigation will decrease sediment loss and thereby also decrease P losses from soils. For example, within the 81,000-ha south-central Idaho Twin Falls irrigation tract, <10% of the land was sprinkler irrigated prior to the 1980s (Bjorneberg et al., 2008). Currently, the tract contains approximately 60% furrow and 40% sprinkler irrigation (Richardson et al., 2008). The tract realized a decrease in net suspended sediment losses from 450 kg ha^{-1} in the early 1970s to 10 kg ha^{-1} in the mid-2000s through the implementation of several management techniques, including replacing furrow with sprinkler irrigation (Bjorneberg et al., 2008). Although soil losses have decreased, changes in soil nutrient status, in particular soil P, may have occurred or continue to occur due to the differences in soil wetting and redox conditions between the two irrigation methods. Such differences may affect soil P dynamics, even in these aridic, calcium

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Abbreviations: EC, electrical conductivity; XANES, X-ray absorption near-edge structure.

carbonate-dominated soils, and thus challenge producers in the face of long-term sustainability as well as stewardship of soil P utilization.

Soils in south-central Idaho are calcareous, containing from 4 to >18% $CaCO_3$ (Leytem et al., 2005; Leytem and Bjorneberg, 2009). In calcareous-dominated soils, it is generally believed that $CaCO_3$ greatly influences P precipitation and that calcium phosphate minerals control P availability (Bohn et al., 1985). Yet this may not be the case if calcareous systems contain other P-reactive constituents such as Fe oxides. For example, Ryan et al. (1985) studied 20 calcareous soils and performed an amorphous Fe extraction test that showed P sorption was strongly related to amorphous Fe oxides instead of $CaCO_3$. Furthermore, calcium minerals may not entirely control P availability in calcareous soils periodically experiencing reduced conditions, such as under furrow irrigation. Under reducing conditions, ferric-bearing P minerals may experience dissolution, releasing P from the mineral matrix and leading to an increase in P availability (Parker and Beck, 2003; Schärer et al., 2009), making P management a true challenge.

Although dissolution of calcium phosphate minerals may indeed be a controlling influence on available P in calcareous soils, the canonical view of soil P dynamics in calcareous soils often neglects the potential impact of P adsorption and desorption from common sorbents such as Fe oxides and calcite (e.g., Holford and Mattingly, 1975; Ryan et al., 1985). Evidence from batch studies and modeling (Millero et al., 2001; Sø et al., 2011) indicates that P can adsorb to calcite in soils and aquatic environments. Phosphorus *K*-edge X-ray absorption near edge structure (XANES) spectroscopy has also provided evidence for calcite as an adsorbent for P (Giguet-Covex et al., 2013). Arai and Sparks (2001) provided spectroscopic evidence for the adsorption of phosphate on Fe oxides as well. Dissolution of phosphate minerals and reductive dissolution of Fe oxide adsorbents are therefore not the only possible P release mechanisms for soils that undergo periodic flooding from furrow irrigation; desorption of P from calcite may also play a role.

If reducing conditions or changes in P adsorption to calcite occur under furrow irrigation, it is possible that soil P dynamics will be different than under sprinkler-irrigated systems. A recent study of the impacts of furrow versus sprinkler irrigation on soil quality by Ippolito et al. (2017) found that furrow-irrigated fields contained significantly greater Olsen-extractable P concentrations (38 mg kg^{-1}) compared with sprinkler-irrigated fields (20 mg kg^{-1}). The almost doubling of Olsen-extractable P under furrow-irrigated fields poses real challenges to producers when faced with strict state P risk indices. The present study was conducted to investigate the influence of furrow or sprinkler irrigation on soil P dynamics, hypothesizing that soil flooding or redox chemistry play a role in increased Olsen-extractable P under furrow irrigation.

Materials and Methods

Producer Experimental Sites

Four paired furrow or sprinkler fields (eight fields total) from four south-central Idaho producers were used, with similar cropping rotations, management practices, and soil series. Typical rotations followed 3 yr of alfalfa (*Medicago sativa* L.)–dry bean or garden bean (*Phaseolus vulgaris* L.)–barley (*Hordeum vulgare* L.)–silage corn (*Zea mays* L.) or sugarsnap pea (*Pisum sativum* L.) or sugarbeet (*Beta vulgaris* L.)–barley. Typical management practices included either fall or spring disking, fall ripping (if necessary), spring roller harrowing, and planting. In the experimental year, each producer grew barley on nearby fields using either furrow or sprinkler irrigation. The quantity of irrigation water used was not determined, nor were crop yields. Furrow irrigation has been in place since the early 1900s in the Twin Falls Irrigation Tract, and sprinkler irrigation has been in place for the past 5 to 8 yr on all four producer fields. Soils at the experimental sites were part of the Minidoka (coarse-silty, mixed, superactive, mesic Xeric Haplodurid), Minveno (loamy, mixed, superactive, mesic, shallow Xeric Haplodurid), Portneuf (coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid), or Sluka (coarse-silty, mixed, superactive, mesic Xeric Haplodurid) soil series, all silt loams, as determined by the Google Earth SoilWeb overlay (University of California, Davis Soil Resource Laboratory, 2008). More detailed information regarding site locations can be found in Ippolito et al. (2017).

Following barley harvest, three soil sampling locations were randomly chosen at the top (the past or current inflow irrigation end depending on sprinkler or furrow irrigation, respectively) and bottom of each field. At each sampling location, 20 soil cores from the 0- to 5-cm depth were collected, composited, air-dried, and ground to pass a 2-mm sieve. Within furrow-irrigated fields, soils were collected and composited from the bed, shoulder, or furrow positions.

Soils were analyzed for pH and electrical conductivity (EC) using a 1:1 soil/deionized water extract (Rhoades, 1996; Thomas, 1996). A soil subsample was pulverized and then analyzed for inorganic carbon (C) content via a modified pressure calcimeter method (Sherrod et al., 2002). Analyses of soil P pools included Olsen-extractable P (Olsen et al., 1954), a modified Hedley sequential extraction for (i) soluble+Al+Fe-bound P (sodium hydroxide extraction), (ii) occluded P (citrate-dithionite extraction), and (iii) Ca-bound P (0.5 M HCl extraction), as described by Kuo (1996). Soil extractions were also performed for total free Al and Fe (Loeppert and Inskeep, 1996) and amorphous Al and Fe (Loeppert and Inskeep, 1996). In addition, soils were analyzed for labile, moderately labile, and nonlabile organic P fractions, as outlined by Zhang and Kovar (2000), as well as for acid and alkaline phosphatase enzyme activity (Tabatabai, 1994).

Significant differences between in-field location (e.g., furrow-irrigated bed vs. shoulder vs. furrow; furrow- or sprinkler-irrigated top vs. bottom of field) were determined at an α of 0.10 using the Proc GLM model in SAS version 9.2 (SAS Institute, 2008). Pearson's correlations were also determined between all measured constituents with significance determined at an α of 0.10 (Steel and Torrie, 1980). An α of 0.10 was used, instead of 0.05, due to the small sample size with respect to the number of producers ($n = 4$) within the size of the entire irrigated watershed (81,000 ha).

To obtain spectroscopic estimates of P speciation, bulk P *K*-edge XANES spectra of soils from the 0- to 5-cm depth from the producer fields were collected on Beamline 14-3 at the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory in Menlo Park, CA. Soils from the furrows at the top and bottom of the fields were further ground

by hand using an agate mortar and pestle; a small quantity of powder from each finely ground, homogenized sample was painted on ultra-low impurity carbon tape (Ted Pella, Inc.) using a synthetic-bristle paintbrush to avoid P contamination. Incident beam energy was selected using a Si(1 1 1) double crystal monochromator in the phi = 90° position, and the beam path was continuously purged with helium. Energy calibration was achieved by setting the top of the primary *K*-edge peak of the lazulite XANES spectrum to 2153.5 eV.

After data collection, multiple spectra were averaged using the SIXPack software package (Webb, 2005). Data normalization and analysis of the bulk P *K*-edge XANES spectra were conducted using Athena (Ravel and Newville, 2005). Linear combination fitting of the normalized P *K*-edge XANES spectra was performed to quantify P speciation in the materials. Standard spectra used for linear combination fitting included apatite diluted 20:1 with confectioner's sugar as described in Massey (2019), and phosphate adsorbed to calcite (Giguet-Covex et al., 2013), which was graciously provided by Charline Giguet-Covex. Fits using other components (e.g., P adsorbed to iron oxides) were examined, but the use of additional components in the linear combination fits could not be qualitatively or quantitatively justified.

Controlled Experimental Site

Following data analyses from the producer experimental sites, it was evident that a more controlled study on soil P transformations under furrow or sprinkler irrigation was warranted. Thus, a randomized complete block design with four replicates was established in a Portneuf silt loam at the Kimberly, ID, USDA-ARS research location, with treatments consisting of either furrow or sprinkler irrigation; these plots were under long-term (>8 decades) furrow irrigation before the experiment. Plots were approximately 150 m long by either 9 m wide (furrow) or 12 m wide (sprinkler). Approximately 20 soil samples were randomly collected and composited within each plot from the 0- to 5-, 5- to 15-, and 0- to 30-cm depths in the spring (before the season's first irrigation event) and fall from 2012 through 2015. Silage corn was grown in the first three cropping seasons, and barley was grown in the fourth cropping season. Nitrogen fertilizer was applied to all plots in all years based on either corn (Brown et al., 2010) or barley (Stark and Brown, 2003) N needs and a preseason soil N test; no P fertilizer was applied in order to monitor soil P transformations over time.

Soils were analyzed for pH and EC, as well as Olsen-extractable P. Also performed were the three-step modified Hedley inorganic P extraction and analysis of amorphous Al and Fe, as previously described for the producer soils. Statistical comparisons were made using *t* tests between the furrow- and sprinkler-irrigated plots in Microsoft Excel at an α of 0.10.

In addition, spectroscopic estimates of P speciation in the controlled experiment soils were obtained using bulk P *K*-edge XANES spectroscopy. Data were collected and analyzed as described above for soils from the producer fields. Since bulk XANES spectroscopy may not always detect minor components, as demonstrated in Massey et al. (2018), microfocused X-ray fluorescence mapping and microfocused P *K*-edge XANES (micro-XANES) were also performed at Stanford Synchrotron Radiation Lightsource Beamline 14-3. Samples were encased in optical epoxy (Epotek 301-2FL), cut to expose soil grains, and lightly polished before analysis. Sample preparation, data collection, and data analysis for micro-XRF and P micro-XANES were similar to the procedures described in Massey (2019).

Results and Discussion

Chemical Analyses and Extractions of Producer Experimental Site Soils

Soil pH (7.8 to 8.0) and EC (0.4 to 0.9 dS m^{-1}) were relatively constant across all producer fields, and no significant differences were observed. For soil pH and EC, as well as other soil measurements, subtle or no differences were observed between furrow-irrigated bed versus shoulder versus furrow position or between the top and bottom of fields under furrow or sprinkler irrigation. Thus, all data from either furrow or sprinkler irrigated sites was combined for subsequent analyses.

Olsen-Extractable P

Furrow-irrigated soils contained more Olsen-extractable P than did sprinkler-irrigated soils (38 versus 20 mg kg^{-1}, respectively; $p < 0.001$; Fig. 1A). Increases in extractable P content have been observed in other periodically flooded systems. Scalenghe et al. (2010) suggested that the onset of reduced conditions can solubilize redox sensitive Fe minerals, simultaneously releasing adsorbed ions, such as P. The authors found a concomitant increase in P and Fe content in calcareous soils undergoing pulsed redox conditions (i.e., 20 d saturated followed by 1 d of oxic conditions and 1 d of drying); Scalenghe et al. (2002) reported similar results for various soils after 1 wk of exposure to redox conditions. Investigators including Pedersen et al. (2006) have documented the release of other sorbed species, such as arsenic (chemically similar to P), on reductive dissolution of Fe oxides. Amarawansha et al. (2015) showed that dissolved reactive P increased by more than 10-fold in some flooded alkaline soils after 1 wk of exposure to redox conditions, and Amarawansha et al. (2016) suggested that seasonally flooded conditions alter soil oxidation–reduction status, leading to changes in soil P status. Differences in Olsen-extractable P between furrow- and sprinkler-irrigated soils suggest that switching from furrow to sprinkler irrigation may be considered a best management practice that decreases elevated available soil P concentrations; this may be especially true for areas like the Twin Falls Irrigation Tract that receive manure land application from the 580,000 dairy cows within close proximity (Idaho Dairymen's Association, 2018). For example, in cropping systems such as those studied herein, the soil Olsen P levels under sprinkler irrigation would suggest adding as much as 90 kg P_2O_5 ha^{-1} for bean and sugarbeet (University of Idaho Extension, 2014), as either dairy manure or inorganic P fertilizer. In contrast, Olsen P concentrations in furrow-irrigated soil approached 40 mg kg^{-1} and, in the state of Idaho, P fertilizer application would be limited to crop removal only, as outlined in the Idaho Nutrient Management Plan (State of Idaho, 2017). Systems such as this pose serious challenges in terms of long-term P management to the point where elevated Olsen-extractable P concentrations under furrow irrigation could limit or eliminate manure land application.

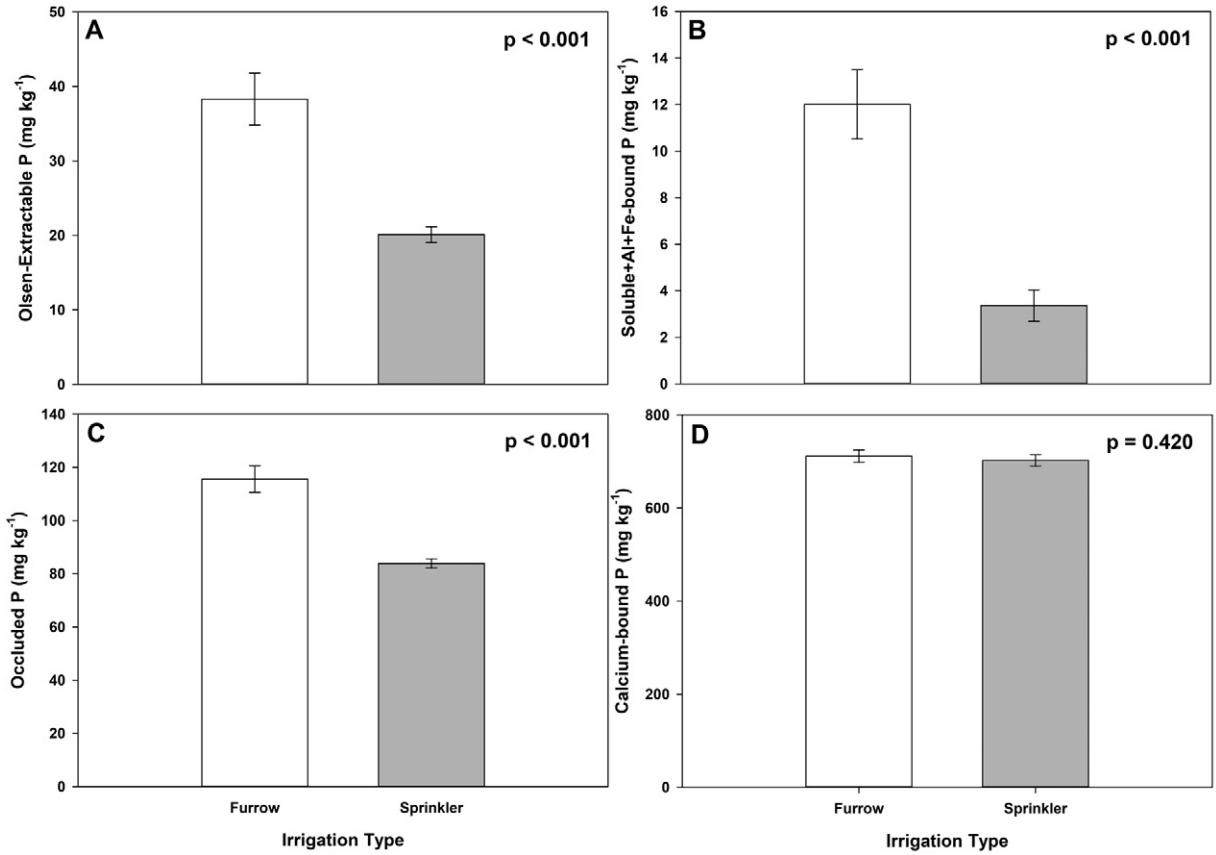

Fig. 1. (A) Olsen-extractable P, and the modified Hedley sequentially extracted, (B) soluble+Al+Fe-bound P (by NaOH extraction), (C) occluded P (by citrate-dithionite extraction), and (D) Ca-bound P (by HCl extraction) pools in the 0- to 5-cm soil depth under furrow or sprinkler irrigation (*n* = 4) from producer experimental sites. Error bars represent one standard error of the mean.

Inorganic P Pools

To understand why differences in Olsen-extractable P were present between furrow and sprinkler irrigation, we performed a modified Hedley sequential inorganic P extraction. Results from the sequential extraction showed greater P concentrations present in the soluble+Al+Fe-bound and occluded pools for furrow-irrigated soils than for sprinkler-irrigated soils (Fig. 1B and C). No differences were detected via sequential extraction between furrow and sprinkler irrigation for the Ca-bound P pool (Fig. 1D), possibly because the 0.5 M HCl extraction may have been unable to distinguish between apatite P and P adsorbed on calcite. Using P *K*-edge XANES spectroscopy (discussed below), differences between apatite P and calcite-bound P were evident under sprinkler versus furrow irrigation. A key limitation to the use of P sequential chemical extraction procedures to study soil P pools is that P pools are operationally defined by the extraction procedures themselves and may not fully reflect the chemical processes occurring at the molecular scale. Nonetheless, chemical extraction data provide permissive evidence that furrow-irrigated soils may have had greater P concentrations associated with Fe phases because of alterations in redox chemistry under furrow irrigation.

Total Free and Amorphous Al and Fe

To clarify whether Fe redox chemistry may have played a role in P release in furrow-irrigated soils, total free and amorphous Al and Fe content were determined. Total free soil Al and Fe content represents 100% of amorphous/poorly crystalline Fe and Al solids, as well as a fraction of crystalline minerals present (van Bodegom et al., 2003), while amorphous Al and Fe content represents only poorly crystalline soil minerals. No significant differences were present between furrow- and sprinkler-irrigated soils for total free Al or Fe (Fig. 2A and B). However, furrow-irrigated soils contained greater amorphous Al and Fe concentrations compared with sprinkler-irrigated soils (Fig. 2C and D).

Aluminum chemistry in soil is not directly affected by redox changes since Al is not a redox-sensitive element at ambient conditions. However, in flooded soils, Al tends to form complexes with organic matter, which may be independent from crystalline minerals (Darke and Walbridge, 2000; Jansen et al., 2011). This could affect soil P chemistry by helping retain P in organic matter–mineral assemblages. In partial support of the contention that amorphous Al may be forming complexes with organic matter, Ippolito et al. (2017) performed a soil quality assessment of the same soils used in the current study and showed that furrow-irrigated soils contained significantly greater soil organic C than did sprinkler-irrigated soils. This organic C can be expected to complex with Al in the soil, thus increasing the amorphous Al fraction, as well as potentially retaining P. Phosphorus associated with organic matter, or in Al-organic matter complexes, may also help to explain the observed behavior in light of the X-ray spectroscopic analyses (discussed below).

As for the amorphous Fe fraction, furrow-irrigated soils likely undergo periods of saturation, causing Fe to be reduced from the trivalent to the divalent state. Under initial reduced conditions, Fe-bearing minerals may dissolve and release both Fe(II) and P to the soil solution, with some P subsequently adsorbed to other

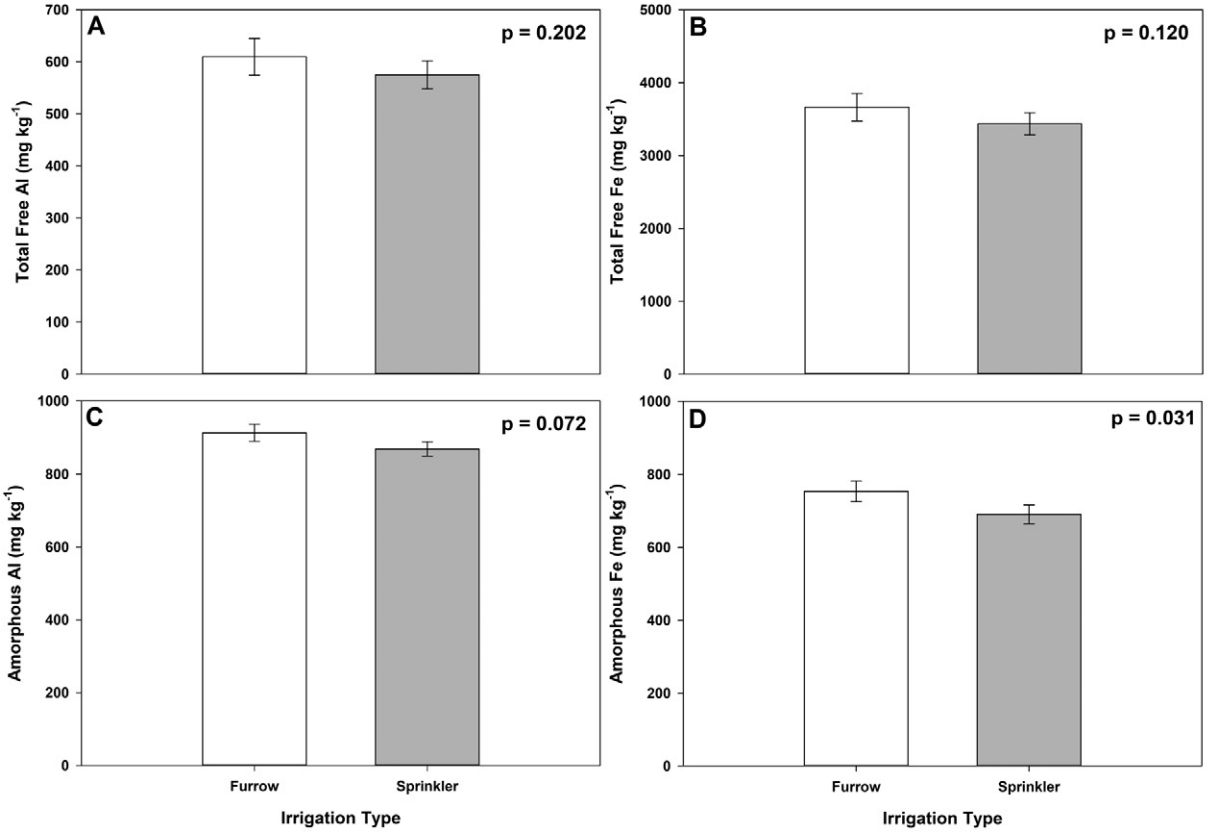

Fig. 2. (A) Total free Al, (B) total free Fe, (C) amorphous Al, and (D) amorphous Fe in the 0- to 5-cm soil depth under furrow or sprinkler irrigation (*n* = 4) from producer experimental sites. Error bars represent one standard error of the mean.

surfaces such as calcite, Al oxides, or other Fe oxides. In part, relatively weak adsorption of P to surfaces such as calcite may have caused the increase in Olsen-extractable P under furrow irrigation compared with sprinkler irrigation. This result is similar to that of González-Alcaraz et al. (2012), who showed that after 3 h of flooding a loam-textured soil, metal oxides released P, which was retained by Ca and Mg compounds. After reductive dissolution and initial P release, soil Fe minerals may undergo further reductive dissolution, which may decrease their crystallinity and concomitantly increase surface area. Alternately, subsequent oxidation of Fe(II) may result in the precipitation of poorly crystalline Fe(III) minerals, also with a high surface area. Increased surface area may have led Fe oxides to sorb greater quantities of P, as also shown by Gumbricht (1993) under reduced conditions. These processes were potentially responsible for the increased P concentrations in the soluble+Al+Fe-bound and occluded sequential extraction steps (Fig. 1A and B). However, the source of P bound to these fractions is unknown based on these data.

In calcareous-dominated soils, it is typically believed that $CaCO_3$ greatly influences P precipitation and that dissolution of calcium phosphate minerals controls P availability. Yet this may not be the case if adsorption is an important factor, especially in calcareous systems that contain adsorbents such as Fe or Al oxides. For example, Holford and Mattingly (1975) studied 24 calcareous soils and observed that P sorption was closely related to total free Fe. It should be noted that the total free Fe extraction procedure also removes 100% of the amorphous Fe phases. Thus, the data of Holford and Mattingly (1975) may actually be describing P sorption onto these phases; the researchers did not perform an amorphous Fe/Al extraction procedure. However, Ryan et al. (1985) studied 20 calcareous soils, performed an amorphous Fe extraction, and showed that P sorption was strongly related to amorphous Fe oxides instead of $CaCO_3$. Jensen and Thamdrup (1993) studied P dynamics in marine sediments (i.e., materials that at some point in time likely were influenced by redox chemistry), suggesting that these sediments may contain P associated with iron minerals. Phosphorus adsorbed to Fe minerals (or other surfaces) would likely be more easily extractable than P mineral precipitates and so may have contributed to the higher Olsen-extractable P observed in these soils.

Organic P Fractionation and Phosphatase Activity

No differences were observed between furrow- or sprinkler-irrigated soil labile organic P content (Table 1). However, furrow-irrigated soil contained greater concentrations of moderately and nonlabile organic P. This may have been due to decreased organic matter mineralization rates under reducing conditions, leading to an accumulation of P in these organic fractions (González-Alcaraz et al., 2012; Zhang et al., 1994). Or, as suggested by Darke and Walbridge (2000), Jansen et al. (2011), and Daugherty et al. (2017), this may have been due to the formation of Al- and/or Fe-organic material complexes under flooded conditions, leading to greater P retention in the moderately labile and nonlabile P pools.

The increases in the moderately labile and nonlabile pools were not reflected in changes in acid or alkaline phosphatase activity. Acid phosphatase activity is known to increase when soils are deficient in P (Margesin and Schinner, 1994; Tarafdar and Marschner, 1994). Acid phosphatase activity can increase due to secretion by plant roots or microorganisms, while alkaline

Table 1. Mean labile, moderately labile, and nonlabile organic soil P and acid and alkaline phosphatase activity in the 0- to 5-cm soil depth under furrow or sprinkler irrigation (standard error of the mean) at producer experimental sites (n = 4).

Producer no. (soil series present)		Irrigation type	Labile organic P	Moderately labile organic P	Nonlabile organic P	Acid phosphatase activity	Alkaline phosphatase activity
			mg kg^{-1}			mg p-nitrophenol kg^{-1} h^{-1}	
1	(Portneuf)	Furrow	10.4 (1.33)	111 (4)	107 (5)	411 (19)	1059 (111)
	(Portneuf, Sluka)	Sprinkler	12.8 (0.45)	104 (3)	103 (4)	471 (8)	1090 (84)
2	(Minveno, Portneuf, Sluka)	Furrow	10.2 (0.36)	110 (7)	108 (4)	397 (14)	1302 (66)
	(Minidoka, Sluka)	Sprinkler	8.00 (0.77)	100 (2)	85 (5)	307 (33)	968 (63)
3	(Minveno, Sluka)	Furrow	12.3 (0.51)	104 (3)	111 (3)	321 (43)	711 (69)
	(Portneuf)	Sprinkler	13.9 (0.49)	85 (10)	110 (4)	279 (9)	810 (14)
4	(Portneuf)	Furrow	12.1 (0.49)	93 (13)	83 (2)	417 (21)	960 (49)
	(Portneuf)	Sprinkler	9.78 (1.05)	81 (4)	83 (2)	492 (19)	1196 (39)
Mean		Furrow	11.2	105	102	386	1008
		Sprinkler	11.1	93	95	387	1016
		p value†	0.840	*0.020*	*0.013*	0.948	0.869

† Significant difference between furrow and sprinkler irrigation ($p < 0.10$) are noted as italicized p values immediately below the means.

phosphatase activity in soil seems derived totally from microorganisms (Tabatabai, 1994). Thus, even though soil P concentration in some (in)organic fractions was lower under sprinkler irrigation than in furrow irrigation, the decreased P did not induce a deficiency response and increase phosphatase excretion by plants or microorganisms.

Correlation Analysis

Pearson's correlations were determined between all chemical and enzyme characteristics for both furrow and sprinkler irrigation (Supplemental Table S1). A focus on correlations between inorganic pools within and between furrow and sprinkler irrigation may provide some insight into the observed Olsen P differences.

Under both furrow and sprinkler irrigation, the Olsen-extractable P significantly correlated with Ca-bound P pools and $CaCO_3$, as would be expected in calcareous systems. However, under furrow irrigation, the Olsen-extractable P also correlated with the soluble+Al+Fe-bound and occluded P pools, which was not the case under sprinkler irrigation. Compared with sprinkler irrigation, furrow-irrigated soils contained ~4 and ~1.4 times as much P in the soluble+Al+Fe-bound and occluded pools, respectively (Fig. 1A and B). If P can be extracted from these pools using Olsen extracting solution, this would likely have significantly contributed to the increase in soil test P values. Supporting this contention, Kuo (1996) stated that an increase in surface negative charge, brought about by the increase in OH^- by the Olsen extracting solution (buffered at pH 8.5), could be responsible for P desorption from Fe oxide surfaces. Furthermore, furrow-irrigated soils contained more P associated with Fe phases. Free OH^- groups could have competed with P (i.e., HPO_4^{2-}) for exchange sites on occluded and amorphous Fe surfaces and released more P into solution during the Olsen extraction.

Chemical Analyses and Extractions of Controlled Experimental Site Soils

Differences in soil pH and EC were observed in the controlled experimental study site (Supplemental Table S2), unlike in the paired producer fields. When significant differences were present, soil pH was always lower (~ 0.1 to 0.3 pH units) and soil EC was almost always greater (0.03 to 1.34 dS m^{-1}) in furrow- as compared to sprinkler-irrigated soils. Ponnamperuma (1972) noted that soil CO_2 accumulation suppresses pH in flooded alkaline soils. More related to the current study, Ponnamperuma (1972) further noted that increased conductance in flooded systems may be due to, among other changes, the release of Fe^{2+} from insoluble Fe^{3+} oxide minerals.

Overall concentrations and differences in Olsen-extractable P were not as great as in the paired producer field experiment (Table 2). The greatest Olsen-extractable P concentrations were

Table 2. Mean Olsen-extractable (i.e. plant-available) phosphorus in the 0- to 5-, 5- to 15-, and 0- to 30-cm soil depths under furrow or sprinkler irrigation (standard error of the mean) at the controlled experimental site (n = 4).

Season	Sprinkler/ furrow	Mean Olsen-extractable P†		
		0–5 cm	5–15 cm	0–30 cm
		mg Olsen P kg^{-1}		
Fall 2012	Furrow	12.7 (1.0)	10.9 (1.3)	9.8 (0.9)
	Sprinkler	12.3 (0.4)	12.7 (0.4)	10.8 (1.0)
	p value†	0.684	0.309	0.565
Spring 2013	Furrow	8.9 (1.6)	9.3 (1.4)	6.4 (0.8)
	Sprinkler	11.0 (1.0)	9.7 (1.0)	7.7 (0.6)
	p value	0.277	0.628	0.135
Fall 2013	Furrow	5.6 (0.9)	6.2 (0.9)	4.6 (0.7)
	Sprinkler	7.0 (0.9)	7.8 (1.1)	5.5 (0.8)
	p value	*0.012*	*0.070*	*0.002*
Spring 2014	Furrow	6.0 (1.0)	6.7 (1.2)	5.6 (0.9)
	Sprinkler	7.5 (0.6)	7.5 (0.6)	7.7 (0.7)
	p value	0.276	0.578	*0.100*
Fall 2014	Furrow	5.8 (0.7)	5.1 (0.8)	5.2 (0.9)
	Sprinkler	7.5 (0.7)	5.6 (0.4)	5.7 (0.6)
	p value	*0.079*	0.498	0.532
Spring 2015	Furrow	4.7 (0.7)	5.1 (0.8)	5.0 (1.0)
	Sprinkler	6.2 (0.6)	6.6 (0.6)	6.0 (0.7)
	p value	*0.023*	*0.038*	0.263
Fall 2015	Furrow	4.3 (0.6)	4.2 (0.7)	4.2 (0.7)
	Sprinkler	5.6 (0.5)	5.4 (0.7)	4.3 (0.6)
	p value	*0.040*	*0.027*	0.928

† Significant difference between furrow and sprinkler irrigation ($p < 0.10$), within a given season/year, are noted as italicized p values immediately below the means.

<13 mg kg^{-1}, and when significant differences were present, Olsen-extractable P was always greater in the sprinkler-irrigated fields compared with furrow-irrigated fields. However, differences never exceeded 1.7 mg kg^{-1} Olsen-extractable P, which certainly did not reach the differences observed in the paired producer field study of ~18 mg kg^{-1}. Furthermore, regardless of irrigation type, both sprinkler- and furrow-irrigated soils would have required identical P fertilizer application rates for corn or barley based on University of Idaho recommendations (Brown et al., 2010; Mahler and Guy, 2007; Stark and Brown, 2003). In this case, one possible explanation for differences in Olsen-extractable P furrow and sprinkler irrigation is that this field had only been recently converted from furrow to sprinkler for the current study. Perhaps several additional years or decades are needed to observe a response similar to that in the above producer study.

As with the paired producer field study, a modified Hedley sequential inorganic P extraction procedure and quantification of amorphous Al and Fe, were performed. Sequential extraction results showed very few differences between furrow and sprinkler irrigation for P associated with soluble+Al+Fe-bound (sodium hydroxide extraction), occluded (citrate-dithionite extraction), or Ca-bound (HCl extraction) P pools (Supplemental Table S3). When differences were present, furrow tended to have greater P concentrations, which was similar to the producer study. Amorphous Al and Fe results showed that in every soil depth when significant differences were present, furrow irrigation contained greater amorphous Al and Fe (Supplemental Table S4). These results match those found in the producer field study, support the correlation between increased conductance and conversion of Fe3+ to Fe2+ as stated by Ponnamperuma (1972), and suggest that given more time, differences indeed might become significant between furrow and sprinkler irrigation in this field.

X-Ray Spectroscopic Analysis of Soil P Species

Phosphorus *K*-edge XANES spectroscopy was conducted to elucidate molecular-scale soil P retention processes under sprinkler and furrow irrigation. Whereas the chemical extractions provided some evidence that P adsorption to Fe oxides may have been important in explaining the observed differences in soil P availability, XANES spectroscopy did not yield clear evidence of Fe-associated P. Spectra from Fe-associated P have a small pre-edge feature, as noted by Beauchemin et al. (2003) and others; this feature was not present in either the bulk P *K*-edge XANES spectra (Fig. 3, Supplemental Fig. S1), or in any spectra collected via micro-XANES spectroscopy (data not shown). Instead, the "shoulder" on the primary peak, as well as characteristic post-edge features, indicated that P in these soils was primarily apatite-like

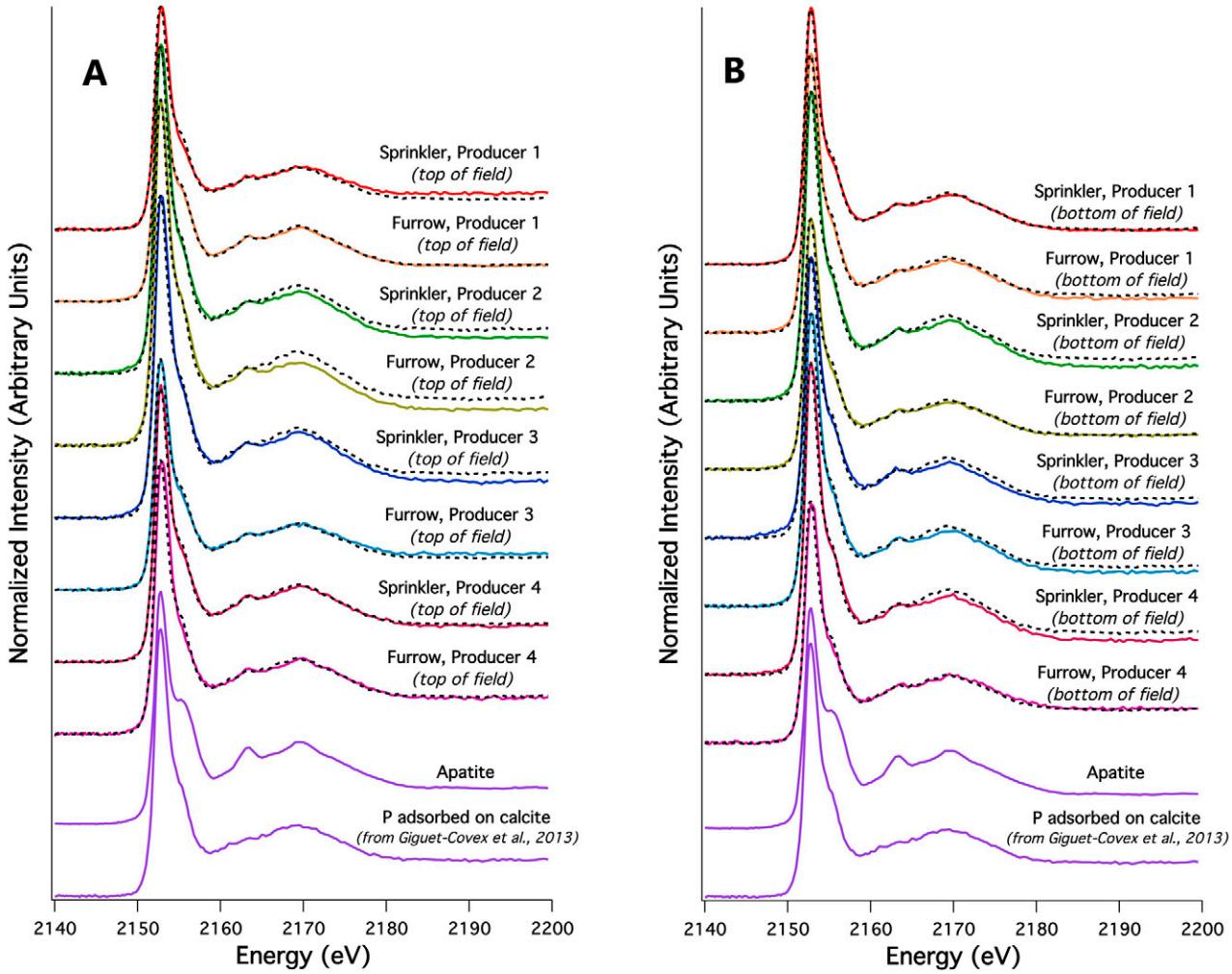

Fig. 3. Bulk P *K*-edge XANES spectra from the 0- to 5-cm soil depth at the (A) top and (B) bottom of fields under furrow or sprinkler irrigation from four producer experimental sites.

(e.g., apatite or octacalcium phosphate, which have very similar spectra), or was adsorbed to calcite (Table 3, Supplemental Tables S5 and S6). Phosphorus adsorbed to calcite has a shoulder feature similar to that of weathered apatite (Ingall et al., 2011), but lacks the post-edge spike that is a prominent feature of apatite-like spectra (Giguet-Covex et al., 2013; Ingall et al., 2011). Although there was no clear trend in soils from the bottom of the producers' fields, linear combination fits of spectra from the soils at the "top" of the field under different irrigation regimes suggested that in three out of four cases, P adsorbed to calcite was actually a greater proportion of soil P under sprinkler irrigation, while apatite-like P was greater in furrow-irrigated soils (Table 3). Fits of spectra from soils at the controlled experimental site yielded similar results to the producer fields, with apatite-like P more common under furrow irrigation and P adsorbed to calcite more common under sprinkler irrigation (Supplemental Fig. S1, Supplemental Table S6). However, the fits of these spectra are not particularly good (Supplemental Fig. S1), so any similarities are speculative at best.

The spectroscopic evidence points to Ca-P minerals/precipitates and P adsorbed to $CaCO_3$ as the primary P species in these soils. This result is in broad agreement with the chemical extraction data, in which HCl-extractable "Ca-bound P" was by far the largest soil P pool (Fig. 1), as expected for calcareous soils. Beauchemin et al. (2003) noted, however, that the detection limit for some P species using P *K*-edge XANES spectroscopy is around 10 to 15 P atom %; Massey (2019) came to a similar conclusion. The observed difference of ~18 mg kg^{-1} Olsen-extractable P was only a few percentage of total soil P (Fig. 1). It is therefore entirely possible that Fe redox chemistry and P adsorbed to Fe oxides were indeed responsible for the observed differences in available P but that Fe-associated P was simply not abundant enough for detection using XANES spectroscopy. In fact, P *K*-edge XANES spectroscopy has been found to underestimate organic P bound to Fe oxides since the characteristic pre-edge feature is less evident or not present (Prietzel and Klysubun, 2018). The same might be true of P adsorbed to Al oxides, or P retained in complexes with Al oxides and organic matter, which yield distinct but relatively featureless XANES spectra that are not easy to distinguish when other P species are dominant. The presence of Fe- or Al-associated P species that were not detected by XANES spectroscopy is therefore a facile and likely explanation for the observed differences in Olsen P, even though there was no strong spectroscopic evidence of Fe-P or Al-P association.

The consistent differences in the P XANES spectra of sprinkler- and furrow-irrigated soils are striking and perhaps not coincidental. If Al oxide- or Fe oxide-bound P is not exerting a controlling influence on available P, the X-ray spectroscopic results may seem counterintuitive: Why would soils with greater amounts of adsorbed P have less Olsen-extractable P? One explanation could be that the spectrum of P adsorbed on calcite in fact represents P that is occluded within calcite, rather than adsorbed on the surface of the mineral (a physical difference that would not necessarily change the electronic structure of P, and thus be invisible in the XANES spectra). The differences in P availability might be explained by greater calcite dissolution or lower calcite surface area and increased crystallinity due to ripening under furrow irrigation. Either of those processes might decrease calcite-bound P, as seen in the spectra and linear combination fits (Fig. 3, Table 3). If P in the soils became more physically accessible, it may also have become more bioavailable.

Taken together, the results from chemical extractions and spectroscopy highlight the methodological challenges associated with studying soil P dynamics. Both methods require assumptions regarding the various pools of soil P represented by the data. Differences in spectra presumably reflect actual differences in soil P species, but interpreting subtle spectral differences can be challenging, even for major species. Similarly, differences in chemical extraction data presumably reflect actual dissimilarities in soil P pools, but a set of assumptions is required to draw conclusions regarding molecular-scale processes on the basis of bulk chemical extraction data (this "leap of faith" seems altogether too common in the scientific literature).

Often, P XANES spectroscopy, chemical extractions, and even other spectroscopic or isotopic methods are used to support and corroborate results when examining soil P behavior (Helfenstein et al., 2018; Prietzel et al., 2016). But what of the case when plausible results do not fully corroborate each other? As noted by Kizewski et al. (2011), the complexity of soil decreases the specificity, and increases the uncertainty, of soil P speciation. And while P *K*-edge XANES spectroscopy can credibly identify relative shifts in major soil P species without the need for the educated guesswork associated with interpreting chemical extraction data, minor species may not be detectable. Additionally, analysis of spectra still requires assumptions and interpretation, which may be incorrect. While the results from chemical extractions and XANES spectroscopy are largely in agreement in the present study, it is notable that unequivocal

Table 3. Phosphorus *K*-edge XANES linear combination fitting results for soils from the top of the producer fields. In all but one case (Producer 4), spectra from sprinkler-irrigated soils had a lower contribution from apatite-like (i.e., apatite, octocalcium phosphate) P and a relatively higher contribution from P adsorbed to calcite. Sums of components in the linear combination fits were normalized to 100%. *R*-factor, χ^2, and reduced χ^2 values were calculated by the Athena software package. Uncertainty, in parentheses, is statistical uncertainty calculated by Athena; total uncertainty was approximately ± 15%.

Producer	Irrigation type	Apatite-like P (P atom %)	P adsorbed to calcite (P atom %)	*R*-factor	χ^2	Reduced χ^2
1	Sprinkler	19% (± 4%)	81% (± 4%)	0.007966	2.0590	0.016877
	Furrow	38% (± 2%)	62% (± 2%)	0.001263	0.4352	0.003567
2	Sprinkler	6% (± 3%)	94% (± 3%)	0.005303	2.9466	0.024152
	Furrow	12% (± 3%)	88% (± 3%)	0.005664	3.5605	0.029184
3	Sprinkler	19% (± 4%)	81% (± 4%)	0.006471	3.5090	0.028762
	Furrow	29% (± 2%)	71% (± 2%)	0.002546	0.7030	0.005763
4	Sprinkler	24% (± 3%)	76% (± 2%)	0.002723	1.0688	0.008761
	Furrow	16% (± 5%)	84% (± 5%)	0.011666	4.6021	0.037723

corroboration between results from different methods is, in this case, difficult. Though differences in soil P pools and speciation between the sprinkler- and furrow-irrigated soils were observed, an unequivocal explanation for the observed changes in soil P behavior remains elusive.

Conclusions

Within paired producer fields, greater Olsen-extractable (i.e., plant-available) P concentrations existed in furrow-irrigated than in sprinkler-irrigated soils. Furrow-irrigated sites underwent longer periods of soil saturation, perhaps leading to reduced conditions. In turn, Fe-bearing minerals may have undergone reductive dissolution, or other biogeochemical processes such as adsorption and complexation of P may have made P more available, leading to the observed increase in Olsen-extractable P. Switching from historical furrow irrigation to current practices of sprinkler irrigation has reduced soil test P concentrations, potentially due to long-term but subtle changes in soil Fe or Ca chemistry. Unfortunately, current methodological limitations of common techniques used to study soil P (e.g., chemical extractions, X-ray absorption spectroscopy) preclude a precise understanding of changes to P dynamics that led to the observed differences. It is clear from these results, however, that changes in P biogeochemistry under varying irrigation regimes can be complex and difficult to interpret. Based on this work, it is clear that challenges and opportunities still exist for us to continue to refine both our understanding of P dynamics, and also the methods used to establish that understanding, to better manage this critical nutrient into the future.

Supplemental Material

Supplemental materials contains Pearson's correlation coefficients for all determined soil characteristics, pH and electrical conductivity, sequential phosphorus extraction, and amorphous Al and Fe data. In addition, P *K*-edge XANES linear combination fitting and spectra results are also presented.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgments

Portions of this research were conducted at the Stanford Synchrotron Radiation Lightsource. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The authors would like to thank S. Webb, B. Kocar, S. Bone, N. Edwards, C. Knotts, D. Day, W. Leonard, and J. Pople for administrative, technical, and operational guidance at Stanford Synchrotron Radiation Lightsource.

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